Electronic Supplementary Information

Light Fueled Rapid Macroscopic Motion by a Green Fluorescent Organic Crystal

Prasenjit Giri,^a Abhrojyoti Mazumder,^a Dibyendu Dey,^a Souvik Garani^a Anju Raveendran^b and Manas K Panda^{* a}

^a Department of Chemistry, Jadavpur University, Kolkata-700032, India. E-mail: <u>mannup25@gmail.com</u>, <u>manaspanda.chemistry@jadavpuruniversity.in</u> ^b KAHM Unity Women's College, Narukara, Mallapuram, Kerala-676122, India

General Procedures:

Materials

4-Acetamido-benzaldehyde and Potassium *tert*-Butoxide were purchased from Sigma-Aldrich and used without further purifications. 3,5-Difluorobenzyl cyanide was purchased from TCI India and was used as received. Tetrabutyl ammonium hydroxide (TBAH) was obtained from Spectrochem. ACS grade (Emplura) solvents were obtained from Merck and was used for synthesis and spectroscopy grade solvents were used for spectroscopy studies.

Instruments & methods:

NMR: ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were carried out on Bruker ASCENDTM 500 & Bruker DPX300 MHz spectrometer using D₆-DMSO as solvent. The chemical shifts (δ) are given in ppm and referenced to the internal standard tetramethylsilane (Si(CH₃)₄).

HRMS: High resolution mass spectra (HRMS) of the compound was recorded by the QTOF Micro YA263 mass spectrometer using electrospray ionization (ESI) mode.

UV-Vis & Fluorescence. Solution and solid-state UV–Vis absorption spectra were recorded on a Shimadzu UV-2401C spectrophotometer. Solid state emission spectra of the crystal samples were recorded on a Horiba Jobin Yvon Fluoromax-4 Spectrofluorometer. The samples were glued on the quartz plate with non-fluorescent grease, placed on optical path and spectra were recorded in front face mode. The E-ArF₂ were sandwiched between two glass plate, placed in the optical path inside a sample holder in the Horiba Fluoromax-4 Spectrofluorometer and data was recorded.

IR Study: IR spectra were recorded in a PerkinElmer LX-1 FT-IR Spectrometer.

Thermal Study: Thermogravimetric analysis (TGA) were performed on a Perkin–Elmer Pyris Diamond TG/DTA in a broad temperature range (between 30°C and 600°C), with heating rate of 10 °C per minute using nitrogen (20 mL/min) as purging gas.

SEM: Scanning Electron Microscopy (SEM) images were obtained from JEOL-JSM5610 instrument using 8-10 kV of energy. Samples were coated with gold prior to the SEM study.

PXRD: Powder X-ray diffraction (PXRD) data of pristine E-ArF₂ and the samples after UV irradiation were carried out in a Bruker D8 advance diffractometer with Cu K α radiation (λ = 1.5418 Å) generated at 40 kV and 40 mA by using 1D position sensitive Lynxeye detector at a scan rate of 0.2 s per step in the range of 2 θ from 2° to 50° under ambient condition.

Single Crystal X-Ray Diffraction:

The single crystal X-ray diffraction data of the *E*-ArF₂ crystals were collected on a Microfocus D8 venture Bruker APEX 3 diffractometer equipped with a CCD area detector and having MoK α radiation ($\lambda = 0.71069$ Å). Data reduction was carried out using SAINT program (v. 8.38A), which were analyzed for agreement using XPREP, all included in the APEX 3 software suite (v 2017.3-0).^{S1} Absorption correction was carried out with the SADABS program.^{S2} The

structure were solved by SHELXT (version 2018/2)^{S3} program of the APEX-3 software suite and refined by refined using SHELXL-2014.^{S4-S6}. All the non-hydrogen atoms were refined anisotropically whereas the positions of H-atoms were calculated and refined isotopically. Crystallographic data of *E*-ArF₂ have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition no 2075638 and the crystallographic parameters are given in Table S1, ESI.

Synthetic Procedure:

Synthesis of ArF2: A 100 mL round-bottom flask equipped with a magnetic stirrer and reflux condenser was charged with 4-acetamidobenzaldehyde (0.143g, 8.8×10^{-4} mol), 3,5-difluoro benzyl cyanide (0.1 ml, 8.8×10^{-4} mol) in 30 mL of methanol solution. Potassium tert-butoxide (0.148g, 1.313×10^{-3} mol) and tetrabutyl ammonium hydroxide (TBAH, 25 % methanol solution, 1.3627 ml, 1.313×10^{-3} mol) was added to it and the resulting mixture was heated at 60 °C for 4 hours. The product was precipitated from the solution which was filtered and washed with methanol and air dried (0.178 g, 68 %). ¹H NMR (500 MHz, CDCl₃): δ (ppm), 10.32 (s, 1H, N<u>H</u>), 8.12 (s, 1H, Ar<u>H</u>), 7.94 (d, 2H, J= 8Hz, Ar<u>H</u>), 7.74 (d, 2H, J= 8 Hz, Ar-<u>H</u>), 7.49 (d, 2H, Ar<u>H</u>), 7.35 (t, 1H, J= 8 Hz, Ar<u>H</u>), 2.10 (s, 3H, C<u>H</u>₃). ¹³C NMR (125 MHz, CDCl₃) δ (ppm). 169.37, 164.28, 164.17, doublet 162.32, 162.21, 145.27, 142.59, 138.30, 131.12, 128.03, 119.25, 118.11, 109.44, 109.22. 105.92, 104.63, 24.63. HRMS: calculated for C₂₉H₁₈F₆N₂ is 298.0918, obtained m/z = 299.0947 (M+H), 321.0763 (M+23). Elemental analysis: calculated for C₁₇H₁₂F₂N₂O; C; 68.45, H; 4.06, N; 9.39, obtained C; 68.71, H; 4.04, N; 9.57.



Scheme S1. Synthetic route to *E*-ArF₂



Figure S1. ¹H NMR spectra of E-ArF₂ in DMSO-d₆ solvent.



Figure S2. ¹³C NMR spectra of E-ArF₂ in DMSO-d₆



Figure S3. High-resolution mass spectra (HRMS) of compound *E*-ArF₂ showing [M+1] peak at 299.0741 and [M+23] peak at 321.0536.



Figure S4. Thermogravimetric analysis (TGA) of *E*-ArF₂ crystal







Figure S6. SEM images of E-ArF₂, (a) before UV irradiation, and (b) after UV irradiation.



Figure S7. Geometrical parameters of *E*-ArF₂ crystal showing distance between two parallel double bonds is 3.871 Å and the obtuse angle is 98.67°. According to Schmidt criteria for [2+2] photocycloaddition, the distance between two parallel double bonds should be below 4.2 Å and the ideal obtuse angle between parallel double bonds is 90°.



Figure S8. ¹H NMR spectra of E-**ArF**₂ after Irradiation in DMSO-d₆ solvent showing the presence of E-**ArF**₂, Z-**ArF**₂ and [2+2] photo dimerized products (E+E and Z+Z dimer).



Figure S9. High-resolution mass spectra (HRMS) of compound E-ArF₂ after Irradiation showing dimer of E-ArF₂ showing [2M+1] at 597.157 where M is the mass of monomer of ArF₂.



Figure S10. Molecular packing of *E*-ArF₂ Crystal viewed along *a*-axis.



Figure S11. Molecular packing of *E*-ArF₂ crystal viewed along *b*-axis



Figure S12. Molecular packing of E-ArF₂ crystal



Figure S13. Absorption spectra of E-ArF₂ in DMF solution before and after UV irradiation.



Figure S14. Overlap plot of experimental and simulated PXRD pattern.



Figure S15. IR spectra of *E*-ArF₂ before and after UV irradiation.

Table S1. Single crystal X-ray parameters of *E*-ARF₂ at 273 K

Chemical formula	$C_{17}H_{12}F_2N_2O$

M _r	298.29
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	3.8711(3)
b / Å	11.1490(10)
<i>c</i> / Å	32.557(3)
α/°	90
$\beta/^{\circ}$	90
γ/°	90
$V/\text{\AA}^3$	1405.1(2)
Zs	4
$ ho_{\rm calc}$ / (g cm ⁻³)	1.410
μ / mm^{-1}	0.108
F ₀₀₀	616
θ_{\min} / °	2.50
$\theta_{\rm max}$ / °	26.94
Reflections collected	48393
Independent reflections	9997
GoF	1.196
Final <i>R</i> indices	$R_1 = 0.0396,$
$[I > 2\sigma(I)]$	$wR_2 = 0.1265$
<i>R</i> indices (all data)	$R_2 = 0.0487,$
	$wR_2 = 0.1410$

References

S1. APEX3, version 2017.3-0, and SAINT, version 8.38A, Bruker AXS Inc., Madison, WI, 2012, URL: <u>https://www.bruker.com</u>

S2. Sheldrick, G. M. SADABS, University of Göttingen, Göttingen, Germany, 1996 (part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, 2017).

S3. Sheldrick, G. M, SHELXTL XT – Crystal Structure Solution, version 2014/4, Bruker AXS, 2010–2014.

S4. Sheldrick, G. M. SHELXL2014. University of Göttingen, Germany, 2014.

- S5. Sheldrick, G. M. Acta Crystallogr. A 2015, 71, 3-8.
- S6. Sheldrick, G. M. Acta Crystallogr. A 2008, 64, 112-122.